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The Ins and Outs of ^{14}C Dating Lead White Paint for Artworks Application

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ABSTRACT: Lead white is known as one of the oldest pigments in art and can be used as a dating material. Upon production following the Stack process, the ^{14}C isotope of atmospheric carbon dioxide is fixed in the carbonate, and its radiocarbon dating can be used as a proxy for the age of a painting. The previously reported carbonate hydrolysis protocol reaches its limitation when confronted with samples presenting a mixture of carbonates, such as lead carbonate (cerussite or hydrocerussite), calcium carbonate (calcite), and/or calcium magnesium carbonate (dolomite). Thermogravimetric analyses indicate that decomposition of lead carbonate can be achieved at 350 °C in TGA diagrams, as other mineral carbonates only decompose to carbon dioxide at temperatures above 700 °C. Thus, a thermal approach is proposed to separate the various carbonates and isolate the specific ^{14}C signature to the lead carbonate. In practice, however, discrepancies between the measured radiocarbon ages and expected ages were observed. FTIR analyses pointed to the formation of metal carboxylates, an indicator that the organic binder is not inert and plays a role in the dating strategy. Upon drying, oxidation and hydrolysis take place leading to the formation of free fatty acids, which in turn interact with the different carbonates upon heating. Their removal was achieved by introduction of a solvent extraction step prior to the thermal treatment, which was confirmed by GC-MS analyses, and thus, the collected carbon dioxide at 350 °C results can be assigned correctly to the decomposition of the lead white pigment. The proposed procedure was furthermore verified on mixed carbonate-bearing paint samples collected from a Baroque oil painting.

In recent studies, the potential of lead white, a mixture of lead carbonates, cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), as a dating material was pushed forward.[1,2] The ^{14}C signature of the carbonate anion was found to be indicative of the time of production. The pigment is formed as a white crust on metallic lead as a result of a corrosion process initiated by the combined action of oxygen, carbon dioxide, water vapor, and acetic acid. Details to the reaction chain can be found in the investigation of Gonzalez et al.,[3] while a historical review on lead white fabrication processes was written by Stols-Witlox.[4] In previous work, the feasibility of using lead white as a proxy for the time of creation of an unattributed painting was performed by dissolving the lead carbonate with phosphoric acid and analyzing the evolved carbon dioxide.[2] The study demonstrated the proof of principle in a pure lead white bearing paint sample; however, it did not explore samples containing mixed carbonates. This left the impression that the approach is relatively straightforward and thus applicable to a much broader spectrum of paintings.

Lead white was a commonly used pigment and thus not the most expensive, but nonetheless, it was economically advantageous to cut the pigment with some filler or extender. Already in the late 18th century, British and Dutch factories were known to adulterate their lead white by the addition of chalk (20%−75%) to cut the costs.[5,6] Other adulterants such as gypsum, barite, or even sand were also employed in different processes.[7] The proportion of these additives was neither regulated nor had it to be declared by the manufacturer. The search for greater whiteness was further explored by the addition of pigmented additives, such as vermilion or smalt to counteract the yellowness of the pigment.[4] Hence, when pursuing the dating of lead white, identifying a sample location containing pure lead white requires thorough analytical prescreening of the sample. In the presence of other carbonates, the accuracy of the results is impaired. Indeed, other carbonate minerals generally carry depleted ^{14}C carbonate anions, which means that dead carbon (i.e., carbon

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essentially free of ^{14}C) is added to the system, and as a consequence, an incorrect result of the lead white pigment's age will be observed. The proposed acidic approach to radiocarbon date lead white therefore reaches its limitation in the presence of other carbonates.

Furthermore, the necessity of taking a sample adds to the challenge. Again, in the initial study, a sample of pure lead white was sought, which required sampling in the center of the pictorial layer. Although the sample was collected in a pre-existing paint crack, such a central sampling location will not be permitted on conservation ethical grounds; minimal invasive sampling along canvas edges is preferable. In her work, Stols-Witlox reviewed the terminology of preparatory layers in oil paintings between 1550 to 1900, and she described multiple formulations with chalk, lead white, and even pigment-based formulations mixed in various binding media such as oil, glue, starch, or casein.[8] In order to make the approach more accessible, the idea was not to target the valuable pictorial layer but rather the preparatory ground layer on the edges of the object, which has an increased likelihood of bearing a mixture of carbonates.

Hence, a selective separation strategy of the different carbonates is necessary. Although chemically alike, mineral carbonates can be separated based on their physical properties, i.e., thermal decomposition temperatures. Upon heating, the carbonates will dissociate and release carbon dioxide under formation of the corresponding metal oxide. Lead white decomposes at around 300 °C, a lower temperature than most other carbonates. In their analysis of lead white used as cosmetics in Egypt and Greece 3000 yrs BC, Beck et al. report a thermal approach.[1] This elegant method which circumvents the problematic presence of the other carbonates does, however, not consider any further interaction of the paint matrix, i.e., the organic binder. Thus, in this study, a methodical investigation regarding the selective separation of lead white from a paint sample for further radiocarbon analysis is reported. In combination with Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and gas-chromatography mass spectrometry (GC-MS), the process was studied in depth, hereby providing an overview of the thermal separation approach for lead white paint dating and the encountered challenges, as well as its limitations.

EXPERIMENTAL SECTION

Materials. *Case Study.* The unattributed half-length female portrait previously dated by ^{14}C analysis of the lead white-bearing paint,[2] shown in Figure 5A, was further investigated since the lead white-bearing paint identified was impure and mixed with other carbonates on the painting edge, which is a more favorable sampling location. This oil on canvas is unsigned and undated, although stylistic assessment suggests a late 17th to a beginning 18th century date, which is supported by ^{14}C analysis of the canvas, binder, and lead white.

Paint Reconstructions. A series of oil mockups with known compositions were examined. Two paint reconstructions bearing enriched and depleted ^{14}C lead white material, one from the MOLART[a] project[9] and the other belonging to the SIK-ISEA in-house collection, were tested. Additionally, modern lead white (HART[b] project[10]) was admixed in various ratios with chalk (Kremer Pigmente GmbH & Co, Aichstetten, Germany) and prepared in linseed oil (Kremer Pigmente GmbH & Co, Aichstetten/Allgäu, Germany, purchased in 2005). Detailed information to the mockups can be found in Table S-1 in the Supporting Information.

Methods. *Lead White Isolation for ^{14}C Analysis.* Sample material was weighed in prebaked glass thimbles (l = 2 cm, Ø = 0.4 cm, Möller, Zurich, Switzerland) and enclosed in prebaked quartz tubes (l = 16 cm, Ø = 0.8 cm, Möller, Zurich, Switzerland), which were sealed under vacuum using a propane/oxygen flame. The sealed tubes were further heated in a muffle furnace (SOLO Industrieöfen GmbH, Bienne, Switzerland). Through cryo-trapping, the produced CO_2 was further transferred to Pyrex tubes (Ø = 0.4 cm, l = 7 cm, Möller, Zurich, Switzerland).[11]

The ^{14}C analyses were conducted on the mini carbon dating system MICADAS at the Physics Department of ETH,[12,13] where a versatile gas interface allows the direct introduction of CO_2 from gas ampules directly to the source.[11,14−16] Standard normalization and a blank correction were performed using the data reduction program BATS.[17] The resulting radiocarbon ages were calibrated using Oxcal v.4.2 software[18,19] with an Intcal13 atmospheric curve.[20]

Complementary Analytical Techniques. FTIR spectra of all samples were collected prior and after the different thermal treatments in order to qualitatively monitor changes in species. The measurements were carried out in transmission mode on a PerkinElmer System 2000 (PerkinElmer, Massachusetts, USA) using a diamond cell to flatten the sample, while attenuated total reflectance (ATR) data was acquired on a PerkinElmer Frontier instrument (PerkinElmer, Massachusetts, USA). Acquisition parameters covered a spectral range from 4000 to 580 cm^{-1} with a resolution of 16 cm^{-1} at 8−16 scans.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were recorded on a TGA/DSC 3+ instrument (Mettler Toledo AG, Greifensee, Switzerland). The measurements were conducted under a nitrogen atmosphere with a heating rate of 33 °C/min from room temperature to 1000 °C. Isothermal experiments were conducted under similar heating conditions, but the temperature was maintained at 350 °C for 2 h.

The individual compounds of the extracted lipid fractions were analyzed using a 7890 gas chromatograph system (Agilent technologies, Santa Clara, CA, USA) coupled to a BenchTOF-select time-of-flight mass spectrometer (Almsco, Llantrisant, UK). For the chromatographic separation, a VF-5 ms capillary column (30 m × 0.25 mm id × 0.25 μm film thickness, Agilent technologies, Santa Clara, CA, USA) was used. The starting temperature for the GC oven was programmed as follows: 40 °C (1 min), 140 °C (at 28.5 °C/min), increased to 320 °C (at 7 °C/min), and then held at 320 °C for 8 min. The samples were at 40 °C in a split mode with a volume of 1.0 μL. Helium was used as the carrier gas at a constant flow of 1.8 mL/min.

RESULTS AND DISCUSSION

TGA Results. Thermogravimetric analyses of pure carbonates display distinct decomposition temperatures (Figure 1), as expected. Lead white, either in cerussite or hydrocerussite form, shows two distinct decomposition steps between 260 and 280 °C and 320−340 °C, respectively, which correspond to literature values.[21,22] The actual decomposition begins at a temperature of 300 °C (onset of the first derivative). Upon isothermal heating at 350 °C during a period of 2 h, only the lead carbonate decomposes to carbon dioxide. In particular, the reaction is complete within the first 15 min. This data shows that in contrary to the work of Beck et al.,[1] who

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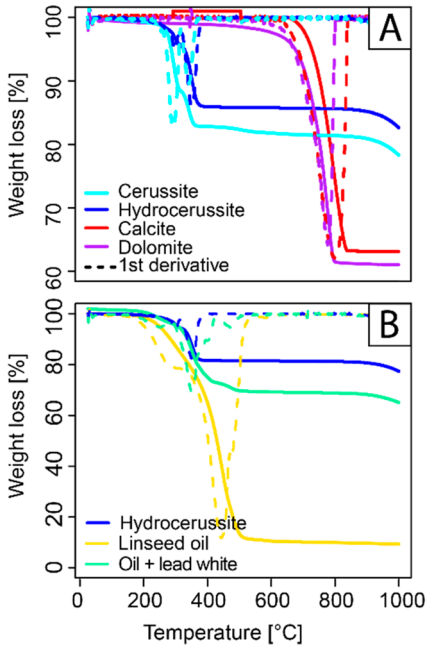

Figure 1. Thermogravimetric curves (continuous lines) and their derivatives (dashed lines) under nitrogen flow as a function of temperature. Analysis of various carbonates (A) in comparison to linseed oil and a paint reconstruction with lead white (B).

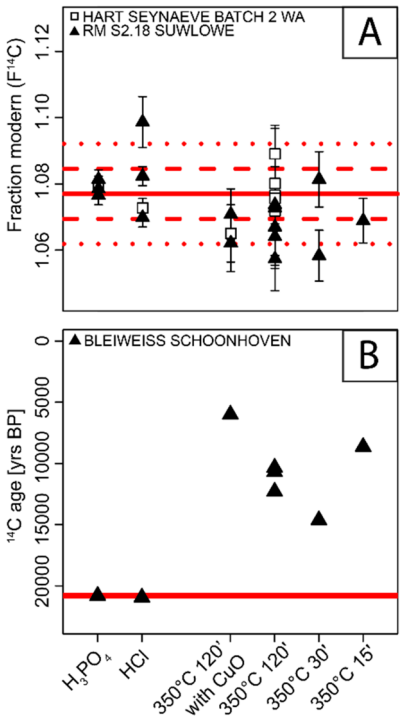

Figure 2. Comparison of different approaches to isolate the ^{14}C signal of lead white pigment (empty squares) and paint mockups (filled triangles). (A) Pigment and oil are contemporaneous. (B) Paint reconstruction bearing a depleted ^{14}C lead white mixed in an oil binder carrying an excess of ^{14}C.

proposes a separation procedure at 400 °C for 2 h, a lower temperature and a shorter reaction time is sufficient. The thermogram of linseed oil shows multiple steps: the first at 150−250 °C which is only noticed in aged oil samples,[23] followed by a first stage of oxidation decomposition between 250 and 400 °C, and finally, pyrolysis above 400 °C.[24]

The thermal behavior of lead white in an oil medium is quite different as already observed by Bonaduce et al. who were the first to characterize the thermal behavior of lead white paint.[25] The resulting thermogram is not a superposition of the two individual compounds with distinct peaks. A first thermal step occurs at 245 °C, with the next at 350 °C, which is followed by multiple steps above 400 °C. On the basis of the peak position, shape, and temperature, the presence of both fatty acids as well as lead carboxylate can be inferred.[25]

Radiocarbon Results. *Pure Lead White.* As shown in Figure 2A, the obtained ^{14}C age of lead white pigment (empty squares) and paint (filled triangles) is unaffected by the sample preparation and delivers consistent ages. Regardless of the procedure, both samples from the HART and MOLART project, where the oil used in paint reconstructions (RM S2.18 SUWLOWE) is contemporary to the lead white pigment, are in agreement with the reference value (red continuous line). While the hydrolysis approach is material specific and independent of any other carbon source, the thermal approach presents the disadvantage that a small percentage of the organic binder also reacts along the decomposition of the lead carbonate and this despite the absence of an oxidizing agent (CuO). The extent of the binder contribution was addressed by dating the Bleiweiss−Schoonhoven sample, which contains ^{14}C-depleted lead white in a ^{14}C-rich oil medium (nuclear bomb test signal). As a result, the ^{14}C age is a mixed signal of both sources yielding a ^{14}C age in the range from 8000 to 15,000 yrs BP. In comparison to previously published data of 20,000 yrs BP, an offset is observed; nonetheless, the distinct signature of depleted ^{14}C material is still noticeable. Depending on the respective reaction time, the oil contribution varies. As illustrated in Figure 2B, within the first 15 min, 20% of the collected carbon originates from the binding media. After 30 min, as more lead carbonate has decomposed, the oil content decreases to 5% and after 2 h to 15%. The carbon contribution from the organic binder was observed to be below 1% of the total sample mass. Under the assumption that the pigment and the organic binder are from the same time period, the oil contribution is not considered to interfere with the lead white dating.

Another point to highlight is the absence of isotopic fractionation during sample preparation, which is critical for ^{14}C measurements as the relative enrichment or depletion of ^{14}C with respect to ^{12}C will cause an age bias. Upon the basis of the presented data, whether isolated by hydrolysis or thermally, the $\delta^{13}C$ value of lead white remains constant. For Stack-processed lead white, the $\delta^{13}C$ ranges between −40‰ to −60‰, which is in good agreement with the $\delta^{13}C$ value for methane which is also produced from fermenting organic material.[26] This is in clear contrast to $\delta^{13}C$ values arising from modern industrial production: the source of CO_2 changed and so does the $\delta^{13}C$, which in the case of Bleiweiss−Schoonoven is from around −25‰ to −30‰, similar to coal products.[26]

Admixed Carbonates. The paint reconstructions prepared with linseed oil (modern) at varying ratios of lead carbonate (modern, Stack process) to calcium carbonate (radiocarbon dead) delivered contradicting results. Surprisingly, an unexpected trend toward older ages was observed. In particular, the higher the calcium carbonate content was, the older the age was, thus indicating that the ^{14}C-depleted calcium carbonate also reacted in some manner. Different temperatures ranging

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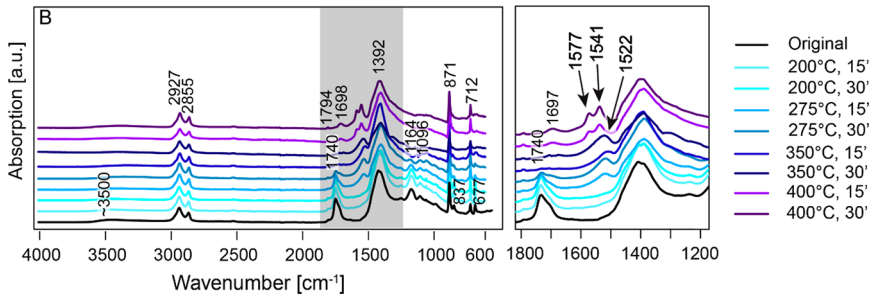

Figure 3. Respective FTIR spectra collected after combustion of paint mockup B at different temperatures and for different reaction times. Full spectrum (left) with zone of interest highlighted in gray and zoomed-in window between 1800 and 1200 cm^{-1} (right).

from 200 to 500 °C showed a similar trend, while shorter reaction times of 15 and 30 min reduced the bias but did not resolve it. The expected $\delta^{13}C$ value of −40‰ was contradicted by a measured value of −25‰, an indication that material with less negative $\delta^{13}C$ is present ($\delta^{13}C_{CaCO_3}$ = 0‰). The $\delta^{13}C$ can therefore be used as an indicator for carbonate contamination, whether undesired $CaCO_3$ contribution occurs or not and thus attests to the reliability of the measurement. Since the same experiment with only powder material did not lead to deviating ages (empty symbols in Figure 4) and displayed coherent $\delta^{13}C$ values, i.e., no calcium carbonate reacted, the bias is linked to the organic binder. This one is typically composed of triglyceride esters of polyunsaturated fatty acids. Partial hydrolysis generates glycerol and free fatty acids, which are potential candidates to react with the carbonate present.

FTIR Results. A deeper understanding of the species formed was brought through FTIR analysis. Figure 3 displays the FTIR spectra collected from mockup B measured after heating the samples at different temperatures for different times (FTIR spectra of all mockups can be found in the SI). The dominant change in all spectra at some point is the loss of intensity of ester bands at 1740, 1164, and 1096 cm^{-1}, respectively, which is characteristic for drying oil.

Indeed lead white, which contains both lead carbonate and lead hydroxide moieties, is not only used by artists for its white color but also because of its excellent drying capabilities.[27] The addition of lead white in paint mixtures promotes the catalysis of oxygen uptake and subsequent decomposition of hydroperoxides to radicals,[28] and it catalyzes the cross-linking steps in the curing process.[29] As a result, a solid cross-linked polymeric network is achieved.[30] Upon heating to 350 °C, the lead carbonate is converted to carbon dioxide and lead oxide, which has similar drying properties to lead white in a paint film and causes the deprotonation of carboxylic acids to form metal carboxylates.[31−33] Moreover, the Pb^{2+} ion is an electron-deficient species and may act as a Lewis acid. By drawing electron density from carbonyl groups, a destabilization occurs which promotes ester hydrolysis.[34] Nonetheless, although lead oxide increases the saponification of ester bonds,[35] its presence alone would not have been sufficient to have caused the disappearance of the ester C═O band. The combined action of heat therefore plays an additional important role. Kinetic studies on a PbO−triolein mixture infer that saponification rates of 80% could be reached in a moisture-free system after 30 min at 180 °C.[36] In the present study, the samples do not reach the same saponification state at the same temperatures. For instance, sample A, which contains a high content of lead white, achieves a state of full saponification after 30 min at 275 °C, while sample B, which contains less lead white, reaches a similar state after 15 min at 350 °C. Sample D composed mostly of calcium carbonate takes much longer to react as little lead white is present. In effect, C═O fully disappears only after reaching temperatures of 400 °C. Moreover, it is known that the heating of esters in a moisture-free system can also lead to the formation of free fatty acids.[37] Triglycerides which possess a β-hydrogen atom may undergo a chelate type 6 atom ring closure by way of a hydrogen bridge.[38] The rearrangement of the ester bond yields an acid and an olefin. However, although in the collected FTIR spectra the characteristic bands for esters all disappear at some point, no carboxylic acid formation is recorded, which would be expected as a result of the hydrolysis of a drying oil polymeric network typically leading to the formation of diacids, glycerols, aldehydes, ketones, and possibly some cross-linked moieties with multiple acid groups. Generally, a broadening of the carbonyl band between 1650 and 1500 cm^{-1} is observed, which suggests that the hydrolysis products have actually reacted further with metal ions to form metal carboxylates.[33,39] This hypothesis is consistent with the study of Keune on reconstructed aged oil paint, who showed by FTIR and secondary ion mass spectrometry (SIMS) analyses that acid groups rapidly react with available metals present as driers.[32] This process also known as metal soap formation is a commonly observed deterioration phenomenon in paintings. Extensive work within the MOLART and De Mayerne research programs provided the first results in characterizing saponification processes in this context.[40]

Generally, an absorption band between 1650 and 1500 cm^{-1} is attributed to carboxylate vibrations. The exact frequency depends on the coordinated metal. A clear identification is not always straightforward due to the shape of the bands. As a result of metal carboxylate formation, the binding media can be described as an ionomer-like system, within which the coordination of the metal ion is not always well defined and causes a broadening of the IR band.[34] In addition, the absorption maximum of two broad and neighboring bands can be difficult to determine due to different concentrations of the species, leading to variable overlap. Although numerous values are reported in the literature for calcium and lead carboxylate IR absorption bands,[33,41−47] they may vary based on the state of the metal soap aggregates, as amorphous metal carboxylate tends to give rise to a broad IR band while the corresponding crystalline metal soap displays sharp COO bands.[48] The formation of saponified products has no defined time frame within a few weeks to a year, with the most important factor being the availability of free fatty acids.[40]

In the present case, the indication of metal soap formation within the network is well visible in sample B (1:1 ratio) in

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Figure 3. Upon heating, a shoulder appears around 1522 cm^{-1}, which can be attributed to lead carboxylates.[41,48] This band grows and broadens with increasing temperature. At 400 °C, two distinct bands appear at 1577 and 1541 cm^{-1}, characteristic for calcium soaps.[42] These observations indicate that $CaCO_3$ is indeed reacting with the matrix and liberates depleted $^{14}CO_2$, leading to the observed bias. Most likely these species are already being formed at lower temperatures in all samples, but due to overlaps with neighboring Pb carboxylates and the broad carbonate band, these are not always visible. On the basis of the measured ^{14}C age and produced amount of CO_2, the dead carbon contribution is calculated to range between 5% and 30%. However, when considering these values with respect to the total amount of the sample material, they correspond to less than 1%. Such little amounts are difficult to identify using FTIR spectroscopy due to overlap with neighboring bands. Generally, upon reaching 400 °C, a shift of the peak maximum at 1522 to a doublet at 1541 and 1577 cm^{-1} occurs, hereby revealing the formation of Ca soaps. This shift is somewhat surprising but can be explained by the thermal behavior of lead white paint. In their study, Bonaduce et al. report the loss of lead palmitate at 400 °C.[25] It is therefore not a shift but rather the decrease of an overlapping band which allows us to detect the Ca species, which are the source of the measured biased ages.

In order to investigate this phenomenon further, a paint reconstruction containing only calcium carbonate in linseed oil was prepared, following the same experimental conditions. Since $CaCO_3$ decomposes to carbon dioxide above 700 °C, only a small fraction of oil was expected to react upon heating at 350 °C for 30 min. The collected CO_2 corresponded to less than 1% of the total sample mass and was thought to carry the age of the linseed oil. An offset was nonetheless observed, indicating that acidic moieties reacted with the calcium carbonate. This result is explained by standard ester hydrolysis which is linked to the oil drying processes. The presence of lead only promotes this reaction, thus increasing the formation of free fatty acids. This observation is consistent with the review by Noble, who states that the time frame for soap formation depends on the availability of fatty acids.[40]

The results from this investigation show that if the temperature is high enough, the carbonate decomposes, and CO_2 is released under formation of a highly reactive metal oxide $M^{II+}O^{II-}$. The cations react immediately with the acids present in the organic binder and form carboxylates, such as lead stearate, which are then very stable under the measuring conditions and no longer evaporate. The evidence from this study suggests that the acids act as "accelerators" on the decomposition of carbonates. In the case of a pure lead white paint layer, the acids have no negative effect on the thermal decomposition and respective carboxylate formation. However, in the case of mixtures of carbonates, i.e., lead white and calcium carbonate, the "accelerating effect" becomes relevant as the experimental conditions are below the destruction temperature of the calcium carbonate temperature. With increasing $CaCO_3$ content, the availability of lead oxide that can bind the acids decreases. The excess acids are therefore free to react with the calcium carbonate, hereby promoting its decomposition and the liberation of depleted $^{14}CO_2$, which is an undesired negative effect. The state of oxidation and polymerization of the organic binder, which is related to the object's age, determines the availability of free fatty acids and thus will influence more or less the isolation of the lead white's ^{14}C age.

Strategy for Removing Low Molecular Weight Acids. By exposing oil paints to an organic solvent, soluble organic components from the paint film can be extracted, in particular, lower molar mass free acids. In his work, Sutherland described the removed compounds as "compounds of the drying oil that have not been chemically incorporated into the polymeric structure of the oil".[49] Under the assumption that free fatty acids are present throughout the paint layer, a solvent extraction step was introduced. The test samples were therefore immersed in either dichloromethane (DCM), acetone, or ethanol prior to the thermal treatment step (Figure 4). After immersion for 24 h, the collected FTIR spectra all

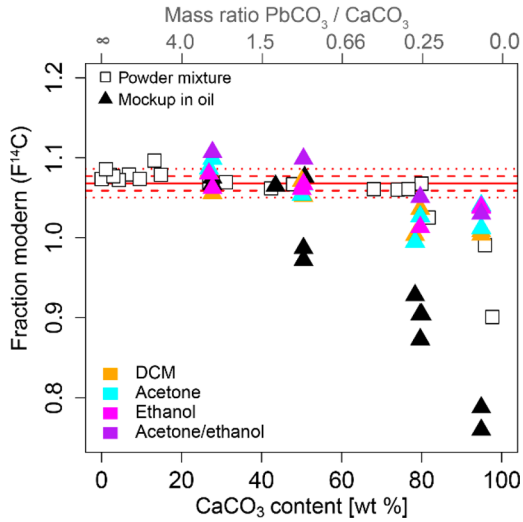

Figure 4. Measured radiocarbon ages for a set of paint reconstructions with a defined calcium carbonate to lead white ratio. The empty symbol represents dry powder mixtures, while the filled triangles represent paint reconstructions. Colored symbols were washed for 24 h in DCM, acetone, ethanol, or both (orange, light blue, pink, or purple, respectively) prior to heating at 350 °C for 30 min, whereas black symbols denote thermal treatment only.

displayed similar features, namely, a general loss of intensity for the oil bands (see Figure S-2 in SI). The respective comparison of the 1740/1400 and 1164/1400 cm^{-1} band ratios indicate a loss of ester functional groups, while the 2920/1400 and 2850/1400 cm^{-1} band ratios hint at a reduction of hydrocarbon chains, i.e., not yet cross-linked binder material. When comparing the spectra after combustion, the aforementioned metal carboxylate bands are no longer visible. The introduction of a solvent extraction step is hereby beneficial in removing free fatty acids and limiting their subsequent availability in future saponification reactions induced through the heating step. To validate the proposed strategy for lead white dating, the nature of the extracted material, i.e., the species which are no longer being formed, required further characterization.

After evaporation of the solvent, the FTIR spectrum of the extract shows a broad carbonyl band at 1740 cm^{-1} as well as a shoulder at 1710 cm^{-1}, which indicates that the mobile material is more degraded (see Figure S-2 in the SI). Either hydrolysis or oxidative fragmentation reactions produce acids, which are not necessarily free fatty acids, but are often still bound to glyceride residues. Their presence within the paint matrix as mobile fraction would explain the observed biased

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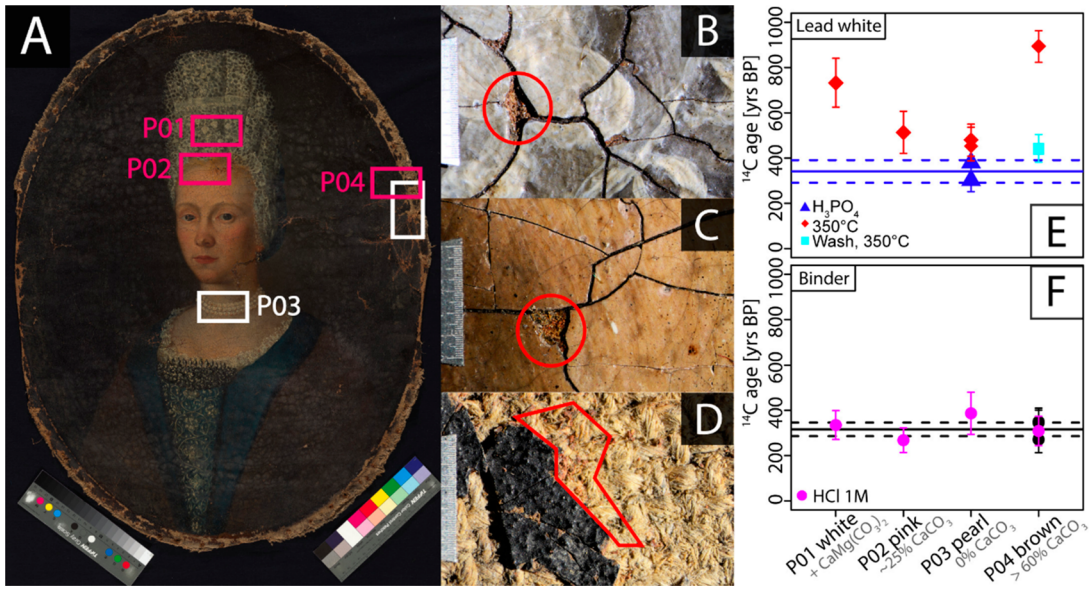

Figure 5. Untitled half-length portrait of a young woman wearing a lace bonnet, pearl necklace, and fur-trimmed cape, unsigned, ca. 17th century, 57 cm × 78 cm, SIK-ISEA (Archive Nr. 171108 0002). Photograph: SIK-ISEA (Philipp Hitz). The previous sampling locations are marked by white boxes, while the new sample sites are indicated in pink. The three details show a close up of the sampling location for samples labeled as P01 white, P02 pink, and P04 brown, respectively (B, C, and D). The scale used represents 5 mm, and the amount of material removed is indicated by the continuous red line. Results of the lead white dating following different procedures (E). Subsequent dating of the organic binder from the same sample (F).

^{14}C age, as they can react with the carbonates and form metal carboxylates, hereby liberating CO_2. Upon derivatization of the extract with SF_4 (spectra not shown here), the broad C═O band can be resolved as the carboxylic acids form acyl fluorides.[47,50] The derivatized sample shows two distinct bands characteristic for both acid and ester groups. In the present case, after immersion of the different paint reconstructions in acetone for 24 h, a net weight loss of 10%−20% was observed, which is more than the typical 7%−13% saturated fatty acid content for linseed oil,[28] thus indicating that other species were also removed. As the oil dries, a complex mixture of fatty acids, glycerol, and glyceride esters as well as partially cross-linked low molecular weight compounds are produced, which are all susceptible to removal by solvent extraction. The exact proportions may vary in function of the paint composition, its curing state, and the solvent extraction exposure time.

Complementary preliminary GC-MS analysis of the solvent extracts indicates the presence of fatty acids derived from the linseed oil binder. The wash extract exhibits free fatty acids, in particular, palmitic and stearic acid, with lower amounts of nonanoic and octanoic acids. Smaller portions of unsaturated fatty acids (oleic) as well as dicarboxylic acid (azelaic) were also found to be washed out by the solvent. These observations corroborate the production of free fatty acids through the drying reaction and hydrolysis induced by the pigment. These in turn react with the metal carbonates present in the paint and as such are the source of the misleading older ages. The choice of the solvent could be further investigated as the mentioned acids are best soluble in cyclic, aprotic solvents.[51] Tetrahydrofuran would therefore perhaps be the most ideal solvent but was not tested here.

In the case of older objects, this negative effect is not expected to be as pronounced as in the model paints. Investigations of 50 year old paint models showed that lead white paint undergoes a net decrease in its ester bands upon drying, and the available fatty acids have since long formed metal soaps.[39,52] Through ageing, the oil binder's reactivity is altered as a result of an ongoing chemical process such as hydrolysis and polymerization. As a result, an increased stabilization of the paint film is observed, and the amount of extractable material, i.e., free fatty acids, is hereby reduced.[49]

While the presence of other carbonates and saponification-induced reactions were addressed in this work, the paint's layer internal reactivity is not yet fully understood. Lead compounds are known to trigger many reactions within a paint layer but their respective reactivity in various situations must still be evaluated, such as the effect of postsynthesis treatment of lead white, changes in the hydrocerussite to cerussite ratio due to pH, or the formation of other species. In particular, in situ lead carbonates can be formed from plumbonacrite ($Pb_5(CO_3)_3O(OH)_2$),[53] or following remineralization reactions,[31−33] their impact on the dating strategy is not yet known and calls for further investigations.

Applied Case Study. In the case of the half-length female portrait, three samples with varying carbonate contents were compared against the previous published data. The relative carbonate content of the sample was quantitatively determined by FTIR spectroscopy (SI Figure S-3). The results from the different treatment procedures are displayed in Figure 5E and summarized in SI Table S-4. As the samples are not pure lead white only, when treated with acid, the resulting ^{14}C ages deviate from the expected value by several thousands of years, which represent a carbonate contamination on the lead white signal of more than 85%. In the thermal approach, the age offset was reduced to several hundreds of years, i.e., 600−1000 yrs BP versus the expected ca. 400 yrs BP, which indicates a residual carbonate contamination of 7%. These observations are linked to the availability of free fatty acids as supported by FTIR acquisition (SI Table S-3). Although metal carboxylates (1514 cm^{-1}) are observed in all samples, the triglyceride network is not yet fully cross-linked, and acid functional groups (1709 cm^{-1}) are still visible. The successive extraction in

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Anal. Chem. 2020, 92, 7674−7682

acetone and ethanol prior to the combustion resolved the issue as demonstrated in Figure 5E. Although no material was left from samples P01 white and P02 pink, the dating of the P04 brown paint collected on the edge of the portrait yields a value of 443 ± 66 yrs BP. This one correlates with the ^{14}C age gained from the pure lead white sample, P03 pearl, for which a mean value of 407 ± 33 yrs was calculated based on the hydrolysis and thermal approach. Thus, 90% of the contamination is hereby removed, and the effectiveness of the solvent extraction step is confirmed as less than 1% residual carbonate contamination remains, which is included in the gas measurement uncertainty. Moreover, following the dating of the lead white, the remaining sample material was further treated with HCl 1 M for subsequent dating of the organic binder. As displayed in Figure 5F, the dating of the binder is much more robust. From the 7 data points, a mean value of 316 ± 24 yrs BP was determined. Owing to variations in atmospheric $^{14}CO_2$ over time, the measured ^{14}C ages require calibration to calendar ages, which for the previously determined mean value extends from the mid-15th to mid-17th century AD and fits the art historical assessment as already reported in Hendriks et al.[2]

These results conducted on aged sample material put the proposed strategy in a more practical context. The altered chemistry of the oil paint is more representative of museum objects, as compared to relatively young model paints.

CONCLUSION

The proposed thermal approach to address the problematic presence of calcium carbonate mixed within lead white-bearing paint highlights the complexity in isolating the lead white's ^{14}C signal. The analytical results confirm that lead white paint decomposes to CO_2 at 350 °C under formation of lead oxide, which in turn reacts with the organic binder and forms lead carboxylates. Experiments carried out on model paints of mixed carbonate content were important in investigating the oil's intrinsic reactivity, i.e., its oxidative properties. The gathered data suggests that the free acid moieties accelerate the carbonate decomposition and hereby liberate carbon dioxide with different ^{14}C signatures. The state of binding media oxidation and polymerization has therefore a critical influence on the ^{14}C dating step for mixtures of carbonates, i.e., lead white mixed with high contents of calcium carbonate. Strong negative effects on the measured ^{14}C ages may be observed if the availability of acids is larger than the formed lead oxide and therefore promote the decomposition of calcium carbonate too.

The prepared paint mockups however do not reflect the altered chemistry of aged oil, where the negative acid effect is expected to be less pronounced as the organic binder has already undergone extensive hydrolysis reactions followed by polymerization. The sample characterization by FTIR spectroscopy is hereby crucial for establishing the state of oil oxidation by identifying the presence of esters, acids, or metal carboxylates as well as the relative carbonate content. FTIR analyses are essential in evaluating the reliability of the results.

In this work, the introduction of a solvent extraction step prior to combustion is proposed as a strategy to limit the negative acid effect and shows to have a positive influence. Moreover, this approach presents the added benefit of removing potential conservation products and should therefore be included as the default step in the sample preparation procedure. The proposed strategy displays enormous potential in the dating of the lead white pigment as the interfering actors have been identified, i.e., free fatty acids. These are naturally deactivated through the formation of carboxylates as the paint film ages but can also be actively eliminated by solvent extraction. As a result, no ^{14}C age bias is expected.

When targeting new dating materials within the pictorial layer, a combination of analytical techniques is essential to gain a deeper comprehensive understanding of the paint material, which will then allow to develop a reliable dating strategy. Only in this way can scientifically educated sampling take place and hereby ensure a meaningful result from the radiocarbon analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.analchem.0c00530.

Additional information summarized in four tables and three figures comprise details of reference material and mockup composition, comparison of FTIR spectra following heat treatment, material characterization of samples collected on case study, and respective ^{14}C results. (PDF)

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Author Contributions

This work is part of L.H.'s PhD thesis work supervised by I.H. Experimental setup was discussed between L.H., E.S.B.F., L.W., D.G., and W.C. M.K. prepared the paint reconstructions. L.H. conducted sample preparation, ^{14}C measurements. and FTIR, with the help of S.Z. for SF_4 derivatization. W.C. directed the

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Anal. Chem. 2020, 92, 7674−7682

TGA measurements. The ensemble of the results was interpreted and discussed among all authors.

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Notes

The authors declare no competing financial interest.

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■ ADDITIONAL NOTES

[a]**Mol**ecular Aspects of Aging in Painted Works of **Art** (1995−2002).

[b]**H**istorically **A**ccurate Oil Painting **R**econstruction **T**echniques (2002−2005). Both projects were led by Professor Dr. Jaap Boon with Dr. Carlyle as the principle investigator and were funded by The Netherlands Organisation for Scientific Research (NWO) and supported by The Netherlands Institute for Atomic and Molecular Physics (FOM-AMOLF) and the Canadian Conservation Institute (CCI).

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